

# PATENT SPECIFICATION

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## (54) PROCESS FOR POLYMERISING AZIRIDINE COMPOUNDS AND INITIATORS FOR USE THEREIN

(71) We, ESPE FABRIK PHARMAZEUTISCHER PRAPARATE G.M.B.H., a German Body Corporate of 8031 Seefeld/Oberbayern, Federal Republic of Germany, do hereby declare the invention for which we pray that Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the polymerisation of aziridines.

Aziridines, which are also known as ethyleneimine compounds, can be converted into high molecular weight polyimine compounds by means of catalysts which open the three-membered ring and thus initiate polymerisation. As a result of these polymerisation initiators, the amino nitrogen of the aziridine ring is cationised and cation chain reaction is started which leads to the polymerisation with formation of the corresponding polyimines as described in more detail in the journal "Farbe and Lacke", 1961, page 71. When monomers are used which contain two or more aziridine groups, cross-linked solid plastics are obtained. Since cationisation of the amino nitrogen of the aziridine ring can take place, for example, in the presence of inorganic or organic acids as well as Lewis-acids, acid esters or other alkylating agents, these substances have been used as polymerisation initiators or hardening agents for diverse aziridine compounds.

German Patent 888,170 discloses the use of neutral sulphuric acid or sulphonic acid esters as initiators for aziridine polymerisation. In Swiss Patent 484,977, a large number of these sulphuric acid or sulphonic acid esters as well as Friedel-Craft's catalysts are listed as suitable for the initiation of polymerisation of aziridine compounds which are used in the production of hardened moulded structures, coatings or adhesive layers of aromatic diethylene imine compounds.

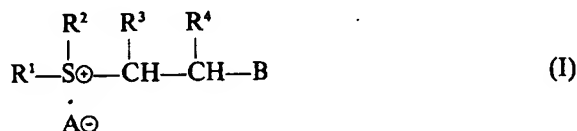
The free inorganic acids have been found impractical because polymerisation achieved with them starts so quickly that there is insufficient time for an even intermixing of the initiator with the monomer compound that is to be polymerized. The weak organic acids, especially those with long organic radicals, on the other hand act too slowly and will rarely lead to a complete hardening and cross-linking.

The alkyl or arylsulphonic acid esters have been used most in practice as initiators. These ester compounds, however, have the disadvantage that they are split already hydrolytically by traces of water, as a result of which the acid is formed, which causes too rapid a polymerization and hardening of the aziridine compounds. Consequently, when these compounds are used as initiators, premature and surprising hardening effects occur whenever the material was not stored completely air tight and dry. Sulfuric acid esters, however, also show additional disadvantages because of their toxic and allergic effects, so that their use in hardening requires particular care. This is particularly important when they are to be used, for example, as polymerization initiators and hardening agents for cross-linkable, organic bifunctional aziridine compounds used in the production of masses for taking impressions of teeth or for dental models.

The so-called onium salts disclosed in the German patent 914,325, such as oxonium, ammonium or sulfonium salts which can also be used for hardening, do not show the above-noted detrimental physiological effects. However, the oxonium salts are even more subject to hydrolysis than the above mentioned esters and it is well known that they can be kept only for a short time at ambient temperature. The ammonium compounds which have been designated as usable, are salts of amines with strong acids which have a relatively short pot time. The sulfonium salts are such sluggish starters that they are practically inactive at

ambient temperature and even at elevated temperatures will relatively slowly introduce polymerisation of the aziridines. Therefore, there still is a need for improving the polymerisation initiating and hardening of aziridine compounds, especially in those cases where they are used in medicine or dental medicine.

It has now been found that certain substituted alkyl sulphonium salts which have at least one hydrogen atom and an electron attracting radical in the carbon atom of the alkyl group in  $\beta$ -position in regard to the sulphur atom, represent particularly suitable polymerisation initiators and hardening agents for diverse mono- and poly-functional aziridine compounds. The polymerisation introduced by these initiators occurs quickly and completely at ambient (or lower) temperature after the period of time required for the mixing and process of the monomer compound that is to be polymerised. These alkyl sulfonium salts correspond to the general formula



in which  $\text{R}^1$  is an alkyl radical of 1 to 18 carbon atoms,  $\text{R}^2$  is an alkyl radical of 1 to 18 carbon atoms or a phenyl alkyl radical with 7 to 18 carbon atoms, wherein said alkyl radicals may contain an ester group and/or ether group, and  $\text{R}^3$  and  $\text{R}^4$  are hydrogen, an alkyl radical of 1 to 18 carbon atoms and/or an aryl radical which can be substituted with a chloro, nitro or alkoxy group, and the alkyl radical  $\text{R}^3$  or  $\text{R}^4$  together with B can form a cycloaliphatic or heterocyclic ring, B represents an electron attracting radical and  $\text{A}^-$  represents a non-nucleophilic anion.

The term "electron attracting radical" means to the man skilled in the art a group of atoms, which causes a withdrawing effect upon the electrons of the neighbored atoms within the same molecule; cf. also E. S. Gould "Mechanismus und Struktur in der organischen Chemie", Verlag Chemie 1962, page 248 f. The term "nucleophilic anion", is also understood in the art as disclosed in the said "Mechanismus und Struktur in der organischen Chemie" textbook, page 307 f., as well as C. G. Swain et al., J. Am. Chem. Soc. 75, page 141 (1953) and A. B. Ash et al., J. Org. Chem. 34, page 4071 (1969) and by the term "non-nucleophilic anion" is meant those anions which are not nucleophilic.

The initiators of formula I can also be used for the hardening of aziridine masses in which the aziridine groups that are to be polymerized are present only in a relatively high dilution. They are of particular advantage for use with the high molecular bifunctional aziridine compounds in dental practice when making impressions or when producing provisional replacement parts for teeth *in situ*, that is, in the mouth cavity, since after a short time of incubation in which the initiator can be completely and homogeneously mixed with the aziridine compound, polymerization and hardening then also starts at room temperature, whereby a quickly and completely hardened product will be obtained.

The sulfonium salts to be used according to the present invention have no disadvantageous effects on the mucous membranes. Also, the polymerization introduced by them is carried completely to an end, so that no residual monomer remains which could possibly cause any irritation or damage to the mucous membranes.

In the sulfonium salts used as a polymerization starter according to the invention, an electron attracting radical B is present on the carbon atom in  $\beta$ -position in relation to the sulfur atom beside at least one hydrogen atom. As a result, this hydrogen atom is properly activated to split off in the presence of the aziridine group as a proton and cationize the nitrogen atom, so that the chain reaction which leads to the hardening of the aziridine compound can start. Since the sulfonium salts are not alkylating agents, their effectiveness can thus not be explained by alkylation of the nitrogen atom of the aziridine group. Carbonyl sulfonyl, nitrile, carboxylic ester or carboxylic amide groups are particularly suitable as electron attracting radicals. The oxygen in the ester or carbonyl groups can also be replaced by sulfur. The phenyl radical may also be utilised although the unsubstituted phenyl radical has a relatively low electron attracting effect. Substitution in the phenyl radical, for example by a chlorine atom or especially by a nitro group, substantially increases the electron attracting effect of the phenyl radical. The nitrile radical is a particularly strong activator so that aziridine compounds contacted with a sulfonium salt activated by a nitrile group harden

relatively rapidly. The customary sulfonium salts which have no such electron attracting radical on the  $\beta$ -C-atom of an alkyl substituent, such as, for example, the well-known diethyldodecylsulfoniumbortetrafluoride have practically no effect as hardening agents for higher molecular weight aziridine compounds. Thus, there is no suggestion in the prior art, that such sulfonium salts substituted in a certain way as disclosed herein are useful in a particularly good and safe manner for the polymerisation of aziridine compounds.

Therefore, a significant contribution for the activation effect of the novel polymerisation starters of the present invention is due to the radical B in  $\beta$ -position in relation to the sulfonium-sulfur atom. This electron attracting radical, also shown in the subsequent examples, can also be component of a cycloaliphatic or heterocyclic ring together with one of the radicals  $R^3$  or  $R^4$  of the formula (I). For example, when B is a sulphonyl group and  $R^3$  or  $R^4$  is an alkyl radical of 1 to 18 C atoms, the alkyl radical of  $R^3$  or  $R^4$  and the  $SO_2$  group of B can form a heterocyclic ring. Thus, in Examples 24, 32 and 34, a sulfonium salt has been used in which the electron attracting  $SO_2$  group is the component of a heterocyclic ring which this group forms together with the radical  $R^3$  of the general formula (I).

Preferred groups for the substituent B are the nitrile and the ester groups. These groups show an intensive electron attracting effect without, however, thereby increasing the hardening speed too greatly, which, as noted above, is undesirable. For  $R^1$  of the formula (I), alkyl radicals with 1 or 2 carbon atoms are preferred, while for  $R^2$ , the preferred alkyl radicals contain from 6 to 18 carbon atoms. An ester group can be present in this radical. Examples for such an ester group-containing radical are the isooctyl acetate or the ethyl laurate radicals as shown in Examples 34 and 35.

Preferred non-nucleophilic anions are the fluoroborate, sulfonate, nitrate, perchlorate, methosulfate or fluorosulfate ion.

The polymerization initiators of the present invention can be used with diverse types of aziridine compounds known in the art such as, for examples, ethyleneimine (aziridine), substituted aziridines and aziridine derivatives (e.g., 2-ethyleneimino-ethanol, N-butyl-ethyleneimine, ethyleneiminosuccinic acid-dimethyl ester, and the like) and other compounds (e.g., polyethers) containing aziridine end groups. Polymerization can be initiated by mixing the polymerization initiator with the aziridine compound at ambient temperature although temperatures above or below ambient may be utilized, if desired. The polymerization initiator may be added in any amount within the skill of the art effective to initiate polymerization.

In the following examples the invention will be explained in more detail using various substituted alkyl sulfonium salts and various aziridine compounds which are to be considered as illustrative of the present invention.

#### EXAMPLE 1.

In 1.0 g of 2-ethyleneimino-ethanol (II), 0.1 g of  $\beta$ -(S-sec-butyl-S-ethylsulphonium)-propionic acid-(2-ethylhexyl)-ester-bortetrafluoride ( $n_D^{20}$ : 1.4498) was dissolved. After the addition of the polymerisation initiator, polymerisation started immediately which was recognisable by a rise in the temperature in a few seconds to about 100°C. After a few minutes, the polyimine had formed as an almost colourless, viscous oil, which is suitable for impregnation of paper in order to impart an increased wet strength to the latter.

#### EXAMPLE 2.

0.02 g of  $\beta$ -(S-lauryl-S-ethylsulphonium)- $\beta$ -phenylpropionic acid-ethyl-ester-bortetrafluoride ( $n_D^{20}$ : 1.4860) was dissolved in 1.0 g of the ethyleneimino compound (II) used in Example 1. Polymerisation started quickly with a temperature rise to about 80°C, and a colourless oil formed in a few minutes which can be used in the same manner as the polymer obtained in Example 1.

#### EXAMPLE 3.

1.0 g of the ethyleneimine compound (II) were reacted with 0.02 g of  $\beta$ -(S-octyl-S-ethylsulphonium)-butyronitrile-bortetrafluoride (III) ( $n_D^{20}$ : 1.4499). In a short time and with a temperature rise to about 75°C, the polyimine formed as a colourless oil. When 0.1 g of the initiator compound (III) was used, the polyimine formed with great heating and a violent reaction as a colourless paste.

#### EXAMPLE 4.

1.0 g of N-butyl-ethyleneimine was mixed with 0.1 g of the initiator compound

III. The temperature rose to about 100°C. After a few minutes, polymerization was completed and the polyimine had developed as a colorless oil.

#### EXAMPLE 5.

1.0 g of ethyleneimino-succinic acid-dimethyl ester was reacted with 0.1 g of the initiator compound III. Polymerization started immediately after the addition of the initiator compound in a violent reaction and the polyimine developed in the form of a bright-yellow rubberlike mass.

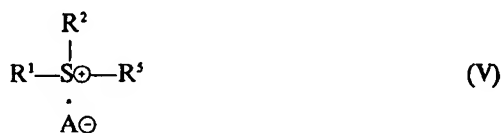
#### EXAMPLE 6.

After mixing of 1.0 g of ethyleneimino-acetic acid-methyl-ester with 0.1 g of the initiator compound III, there is obtained practically instantaneously in a violent reaction the polyimine as a tough, bright-brown mass.

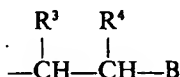
#### EXAMPLE 7.

0.02 g of the initiator compound III was stirred into 1.0 g of 2,2-bis-(p-β-hydroxy-ethoxy-phenyl)-propane-bis-α-ethyleneimino-propionate (IV). Gelling and hardening began quickly so that after about 1 minute, a very hard cross-linked polyimine product had formed.

In the following Table 1, Examples 8 to 24 are summarized. Each of these Examples was carried out in the same manner as described in Example 7 with the bifunctional aziridine derivative IV used and, with the use of various sulfonium salts of the formula V



as polymerization initiator, in which the radical R<sup>3</sup> stands for the group



of the formula (I). In the third to the last column, the refractive index (n<sub>D</sub><sup>20</sup>) or the melting point for each sulfonium salt used, is given. The two last columns of Table 1 give for the individual Examples in how many minutes after the addition of the sulfonium salt the gelling started or the polymerization and hardening was essentially ended.

Most of the sulfonium salts mentioned in the examples are oils at ambient temperature and it was possible to mix them in as such directly into the aziridine derivatives. The sulfonium salts which are solid at ambient temperature, (and the melting points of which are given in the third to the last column of Table 1) were dissolved in a ratio of 1:2 in sulfolane or propylene glycol-carbonate-1,2, and this solution was then admixed with the aziridine to be hardened.

In the Tables "sulfolanyl" means the radical of formula:

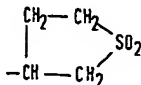


TABLE 1

Example No.	Sulfonium Salt (V) Weight percent	R <sup>1</sup>	R <sup>2</sup>	R <sup>S</sup>	A <sup>⊖</sup>	n <sub>D</sub> or melting point	Gelling Time (min)	Hardening Time (min)
8	2.4	C <sub>2</sub> H <sub>5</sub>	C <sub>12</sub> H <sub>25</sub>	-CH <sub>2</sub> -CH <sub>2</sub> -COOC <sub>8</sub> H <sub>17</sub>	BF <sub>4</sub>	1.4522	2.5	5
9	5	CH <sub>3</sub>	"	"	Methosulfate	1.4702	5	20
10	2	C <sub>2</sub> H <sub>5</sub>	sec-C <sub>4</sub> H <sub>9</sub>	"	BF <sub>4</sub>	1.4498	2.5	3.5
11	5	CH <sub>3</sub>	C <sub>12</sub> H <sub>25</sub>	-CH <sub>2</sub> -CH <sub>2</sub> -COOC <sub>2</sub> H <sub>5</sub>	Methosulfate	28°C	3.5	5
12	8	"	"	"	2,5-Dichloro-benzenesulfonate	1.5190	3	6
13	2	C <sub>2</sub> H <sub>5</sub>	sec-C <sub>4</sub> H <sub>9</sub>	"	BF <sub>4</sub>	1.4440	2	3.5
14	1.4	"	C <sub>12</sub> H <sub>25</sub>	-CH <sub>2</sub> -CH <sub>2</sub> -COO-C <sub>2</sub> H <sub>4</sub> -O-C <sub>2</sub> H <sub>5</sub>	BF <sub>4</sub>	1.4495	2.5	4
15	4	CH <sub>3</sub>	C <sub>4</sub> H <sub>9</sub>	-CH <sub>2</sub> -CH <sub>2</sub> -COOC <sub>2</sub> H <sub>5</sub>	2,5-Dichloro-benzenesulfonate	1.5355	3.5	5
16	1.7	C <sub>2</sub> H <sub>5</sub>	C <sub>12</sub> H <sub>25</sub>	-CH <sub>2</sub> -CH <sub>2</sub> -COOCH <sub>3</sub>	BF <sub>4</sub>	1.4492	2.5	4
17	1.7	"	"	$\begin{array}{c} \text{CH}_3 \\   \\ -\text{CH}-\text{CH}_2-\text{COOCH}_3 \end{array}$	BF <sub>4</sub>	1.4524	2.5	3.5

TABLE 1 (Continued)

Example No.	Sulfonium Salt (V) Weight percent	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	A <sup>⊖</sup>	n <sub>D</sub> 20 or melting point	Gelling Time (min)	Hardening Time (min)
18	3	C <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>13</sub>	CH <sub>3</sub>   -CH <sub>2</sub> -CH-CN	BF <sub>4</sub>	1.4492	5.5	8
19	6	"	C <sub>8</sub> H <sub>17</sub>	"	BF <sub>4</sub>	1.4491	4	6
20	3	"	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub>	"	BF <sub>4</sub>	42°C	3.5	4.5
21	5	"	2-C <sub>2</sub> H <sub>5</sub> -C <sub>6</sub> H <sub>12</sub>	"	BF <sub>4</sub>	1.4523	3	5.5
22	4	"	C <sub>12</sub> H <sub>25</sub>	-CH <sub>2</sub> -CH <sub>2</sub> -CO-N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	BF <sub>4</sub>	1.4621	2	10
23	2	"	"	-CH <sub>2</sub> -CH <sub>2</sub> -CO-C <sub>6</sub> H <sub>5</sub>	BF <sub>4</sub>	1.4881	0.5	1
24	1.5	"	"	sulfolanyl	BF <sub>4</sub>	75°C	1.3	2

1.0 g of a polyether with aziridino end groups (VI), having an average molecular weight of about 6500 and the production of which is described in the German patent 1,745,810 is mixed with 0.1 g of  $\beta$ -(S-lauryl-S-ethyl-sulfonium)-propionic acid-(2-ethyl-hexyl)-ester-fluoborate ( $n_D^{20}$ : 1.4522). After about 6 minutes, gelling starts and after about 45 minutes a rubber-elastic, solid mass has developed.

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In the following Table 2, Examples 26 to 35 have been summarized. All of these examples have all been carried out with the aziridine derivative (VI) of Example 25 and with the use of the stated sulfonium salts of the formula (V) as a polymerization initiator. In Table 2, in the third to the last column, the refractive index ( $n_D^{20}$ ) or the melting point of the sulfonium salt used is given. The two last columns state the time for gelling to occur after the mixing and the time polymerization concluded and a dust-dry, solid rubber-elastic mass had developed.

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TABLE 2

Example No.	Sulfonium Salt (V) weight percent	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	A <sup>-</sup>	n <sub>D</sub> <sup>20</sup> or melting point	Gelling Time (min)	Time, polymer formed in rubber-elastic product (min)
26	20	C <sub>2</sub> H <sub>5</sub>	C <sub>12</sub> H <sub>25</sub>	-CH <sub>2</sub> -CH <sub>2</sub> -COO-C <sub>2</sub> H <sub>4</sub> -O-C <sub>2</sub> H <sub>5</sub>	BF <sub>4</sub>	1.4495	5	40
27	2	"	"	CH <sub>3</sub>   -CH-CH <sub>2</sub> -CN	BF <sub>4</sub>	1.4565	2	8
28	7	"	C <sub>6</sub> H <sub>17</sub>	-CH <sub>2</sub> -CH <sub>2</sub> -CN	BF <sub>4</sub>	1.4487	2.5	8
29	5	"	C <sub>12</sub> H <sub>25</sub>	"	BF <sub>4</sub>	63°C	2.3	8.5
30	3	"	"	C <sub>6</sub> H <sub>5</sub>   -CH-CH <sub>2</sub> -CO-N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	BF <sub>4</sub>	35°C	0.5	2
31	2.5	"	"	-CH <sub>2</sub> -CH <sub>2</sub> -CO-C <sub>6</sub> H <sub>5</sub>	BF <sub>4</sub>	1.4881	2	10
32	20	"	"	sulfolanyl	BF <sub>4</sub>	75°	5	12
33	7	"	"	m-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>   -CH-CH <sub>2</sub> -COOC <sub>2</sub> H <sub>5</sub>	BF <sub>4</sub>	1.4948	2	4
34	3	"	2-C <sub>2</sub> H <sub>5</sub> -C <sub>4</sub> H <sub>9</sub> -OOC-CH <sub>2</sub>	sulfolanyl	BF <sub>4</sub>	49°	1.5	6
35	6	"	C <sub>11</sub> H <sub>23</sub> COOC <sub>2</sub> H <sub>4</sub>	CH <sub>3</sub>   -CH-CH <sub>2</sub> -CN	BF <sub>4</sub>	1.4647	1.5	4.5



## EXAMPLE 36.

An ethyleneimine preparation usable for the production of dental replacement parts was produced as follows:

100 g of the ethyleneimine compound (IV) was kneaded together with 35 g of nylon powder ( $<60\mu$ ), which serves as a filler and was colored similarly to the color of teeth by the addition of cadmium sulfide pigment.

For the production of a semipermanent bridge, 7 g of this paste was mixed with 0.3 g of the sulfonium salt of Example 19 and the mixture was inserted into an alginate impression which had been obtained prior to the preparation of the pillar teeth and in which a connecting groove had been cut between the impressions of said pillar teeth. Immediately thereafter, the impression was replaced into the mouth of the patient. After the beginning of hardening, the impression together with the hardening molded body was taken from the mouth and allowed to harden for about 10 minutes. Subsequently, the provisional bridge was finished in the customary manner by removal of the excess and polishing.

## EXAMPLE 37.

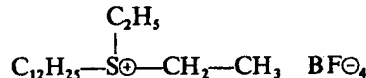
For the production of a mass for taking impressions for dental purposes, 800 g of the bifunctional ethyleneimine compound (VI), of Example 25, was kneaded together with 150 g of fine diatomaceous earth to form a paste. 30 g of the paste was mixed with 2% of the sulfonium salt of Example 31 and the mixture was immediately inserted with a suitable tray into the mouth of the patient. After about 10 minutes, the impression was taken out. A dimensionally-stable but rubber-elastic impression of the part of the mouth that is to be copied was obtained.

## COMPARATIVE EXAMPLE.

The surprising effect of the sulfonium salts used in the present invention is shown by the following comparative experiments in which a customary sulfonium salt was also used as a polymerization initiator for aziridine derivatives.

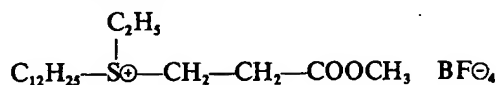
The bifunctional aziridine derivatives IV or VI respectively, used in Examples 8 to 24 (Table 1), and 26 to 35 (Table 2) were used as well as the following sulfonium salts:

(1) A sulfonium salt known in the prior art:

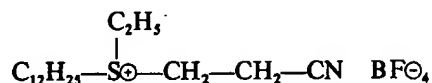


(polymerization initiator VII)  
(melting point:  $48.5^\circ\text{C}$ )

and (2) sulfonium salts of the present invention:



(polymerization initiator VIII),  
oil ( $n_D^{20}$ : 1.4492)



(polymerization initiator IX),  
solid, melting point:  $63^\circ\text{C}$

As can be seen from the formulae, the three sulfonium salts used here as polymerization initiators have a very similar composition. The two polymerization initiators of the present invention (VIII and IX) differ from the conventional sulfonium salt (VII) through the presence of an ester or nitrile group additionally present as an electron attracting radical on the carbon atom in  $\beta$ -position in relation to the sulfur atom.

In these experiments, each of the sulfonium salts were added to the aziridine derivatives in a quantity of 5% by weight. The sulfonium salts were first dissolved

in twice the weight of sulfolane and were added in the form of the solutions.

The following results were obtained:

In *experiment A* utilizing the sulfonium salt of the prior art (VII), and using the aziridine compound IV, no change was recognizable after 1 hour at ambient temperature. Even after an additional 2 hours at 50°C, no change of the mixture was recognizable.

Similarly, in *experiment B*, which was carried out with the substances VI + VII, no change was found after 1 hour at ambient temperature and after 2 additional hours at 50°C.

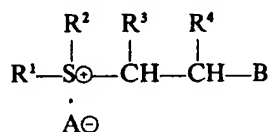
In *experiment C*, carried out according to the present invention and using the substances IV + VIII, complete hardening of the mixture occurred after 3 minutes at ambient temperature.

Also, in *experiment D*, which was carried out using the substances VI + IX, the cross-linking into a rubberlike mass had been completed within 8 minutes at ambient temperature.

Thus it is proven that known sulfonium salts are unsuitable as starters for the polymerization of aziridine derivatives. Even at 50°C, they are completely ineffective. The alkyl sulfonium salts of the formula I on the contrary, trigger a quick polymerization even at ambient temperature, which is essentially completed within a few minutes.

#### WHAT WE CLAIM IS:—

1. A process for the production of an aziridine polymer which comprises mixing an aziridine compound with a polymerization initiator having the formula:



where R<sup>1</sup> is an alkyl radical of 1 to 18 C atoms, R<sup>2</sup> is an alkyl radical of 1 to 18 C atoms or a phenyl alkyl radical of 7 to 18 C atoms, and said alkyl radicals may contain an ester group and/or ether group, R<sup>3</sup> and R<sup>4</sup> are hydrogen, an alkyl radical of 1 to 18 C atoms and/or an aryl radical which can be substituted with a chloro, nitro or alkoxy group, and the alkyl radical of R<sup>3</sup> or R<sup>4</sup> together with B can form a cycloaliphatic or heterocyclic ring, B is an electron attracting radical, and A is a non-nucleophilic anion.

2. The process of claim 1 wherein R<sup>1</sup> is methyl or ethyl.

3. The process of claim 1 or 2 wherein R<sup>2</sup> is an alkyl radical of 6 to 18 C atoms.

4. The process of claim 1, 2, or 3 wherein R<sup>3</sup> and R<sup>4</sup> are each alkyl radicals of 1 to 18 C atoms.

5. The process of any of claims 1 to 4 wherein B is a carbonyl, sulphonyl, nitrile, ester or amide group.

6. The process of claim 5 wherein B is a sulphonyl group, R<sup>3</sup> or R<sup>4</sup> is an alkyl radical of 1 to 18 C atoms, and the alkyl radical of R<sup>3</sup> or R<sup>4</sup> and the SO<sub>2</sub> group of B form a heterocyclic ring.

7. The process of any of claims 1 to 6 wherein A is a fluoroborate, sulphonate, nitrate, perchlorate, methosulphate or fluorosulphate ion.

8. The process of any of claims 1 to 7 wherein the aziridine compound and the polymerisation initiator are mixed at ambient temperature.

9. The process of claim 1 substantially as described in any one of the foregoing Examples.

10. An aziridine polymer when produced by the process of any of claims 1 to 9.

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